Organometallics **1998,** *17,* 5445−5447 5445

Bridged Phospholyl−Amido Titanium Catalysts for Ethylene Polymerization

Steve J. Brown,[†] Xiaoliang Gao,[†] Daryll G. Harrison,[†] Linda Koch,[†]
Rupert E. v. H. Spence,*,[†] and Glenn P. A. Yap[‡]

NOVA Research & Technology Corporation, 2928 16th Street NE, Calgary,
Alberta, Canada T2E 7K7, and Department of Chemistry, University of Windsor,
Windsor, Ontario, Canada N9B 3P4

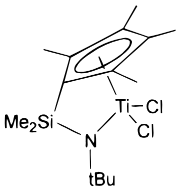
Received September 15, 1998

Summary: The preparation, characterization, and an X-ray crystal structure for the first examples of covalently bridged phospholyl complexes of titanium are reported. Preliminary ethylene polymerization data for the ansa phospholyl−amido titanium complexes show catalyst activities comparable to the well-known bridged cyclopentadienyl−amido titanium constrained geometry catalysts.

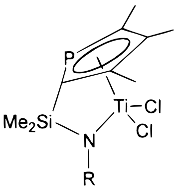
The commercialization of the group 4 metallocenes for olefin polymerization has spurred the search for new ligands that will support single-site catalyst activity in the early transition metals. One direction has been to explore 6π-electron heterocyclic ligands that bind to the metal in a fashion similar to the cyclopentadienes. For example, group 4 metal π-complexes with boron−carbon,[1] boron−nitrogen−carbon,[2] and phosphorus−carbon[3,4] heterocyclic ligands have been examined for catalyst activity. Of these ligands, the phospholyls, being readily accessible[5] and electronically[4] similar to cyclopentadienyl, perhaps have the greatest opportunity for yielding commercially useful catalysts. Consistent with this view, the phospholyl catalysts have been one of the most industrially[3] and academically[4] studied alternatives to metallocenes, despite potential problems brought by the Lewis basic phosphorus atom.[4]

Optimization of catalyst performance by manipulation and design of the cyclopentadienyl ligand has been key to the success of the metallocene catalysts. Optimization of the phospholyl catalyst will require equally careful ligand design. One way to achieve this is to apply ligand technologies created for the metallocenes to the phospholyl catalysts.

In metallocenes, introduction of a bridge to form chelating ligands can lead to substantial improvements in catalyst performance. In particular, the presence of a bridge in the well-known constrained geometry catalysts **1** leads to large catalyst activity increases over most unbridged monocyclopentadienyltitanium complexes.[6] Exploiting this result, we report the preparation, characterization, and ethylene polymerization properties of the novel *ansa* phospholyl−amido titanium complex, **2**, a system structurally similar to catalyst **1**. Compounds **2** are the first examples of covalently bridged phospholyl catalysts.[7]



1



2

The preparation of compounds **2** involved a blend of high yielding synthetic methods employed in phosphole and metallocene chemistry (Scheme 1). These methods generally eliminated the need for significant purification of the synthetic intermediates.[8] Using zirconocene-coupling methods,[9] sequential treatment of Schwartz's reagent with 2-butyne, MeLi, and MeC≡CSiMe$_2$Cl (generated from propynylmagnesium chloride and Me$_2$SiCl$_2$) gave zirconacycle **3** in 69% yield after crystallization from hexane. As expected, on the basis of the reductive coupling results reported for Me$_3$Si-substituted alkynes,[10] only the α Me$_2$SiCl-substituted regioisomer of **3** was obtained.

Heating compound **3** with 1 equiv of PhPCl$_2$ in toluene gave phosphole **4** as an oil in essentially

---

[†] NOVA Research & Technology Corporation. E-mail: spencer@novachem.com.

[‡] University of Windsor. Current address: University of Ottawa.

(1) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Bazan, G. C.; Donnelly, S. J.; Rodriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671. (c) Krishnamurti, R.; Nagy, S.; Etherton, B. P. (Occidental) World Pat. Appl. 96/23004, 1996.

(2) Nagy, S.; Krishnamurti, R.; Etherton, B. P. (Occidental) World Pat. Appl. 96/34021, 1996.

(3) (a) Sone, M.; Yano, A. (Tosoh) Eur. Pat. Appl. 0574794, 1993. (b) de Boer, E. J. M.; de Boer, H. J. R.; Heeres, H. J. (Shell) World Pat. Appl. 95/04087, 1995. (c) Yokota, K. (Idemitsu Kosan) Eur. Pat. Appl. 590486, 1994. (d) Aoki, T.; Kurashiki-shi, O. (Asahi Kasei) Eur. Pat. Appl. 617052, 1994. (e) Sugano, T.; Yamamoto, K. (Mitsubishi Chemical) Eur. Pat. Appl. 7287773, 1996. (f) van Beek, J.; van Doremaele, G. H. J.; Vandewiele, K. A.; van den Winkel, Y. (DSM) Belg. Pat. Appl. 9300710, 1995. (g) De Boer, E. J. M.; De Boer, H. J. R.; Heeres, H. J. (Union Carbide) U.S. Pat. 5756417, 1998; (h) de Boer, E. J. M. Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A: Chem.* **1998**, *128*, 155.

(4) (a) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lentz, D.; Budzelaar, P. H. M. *Chem. Ber.* **1996**, *129*, 1517. (b) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann, R.; Hahn, E. *J. Organomet. Chem.* **1995**, *501*, 219.

(5) (a) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(6) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. E. (Dow Chemical Company) Eur. Pat. App 0416815 A2, 1991. (b) Stevens, J. C. *Catalyst Design for Tailor-made Polyolefins, Studies in Surface Science and Catalysis*, Vol. 89; Soga, K., Terano, M. Eds.; Elsevier: Amsterdam, 1994; pp 277−284.

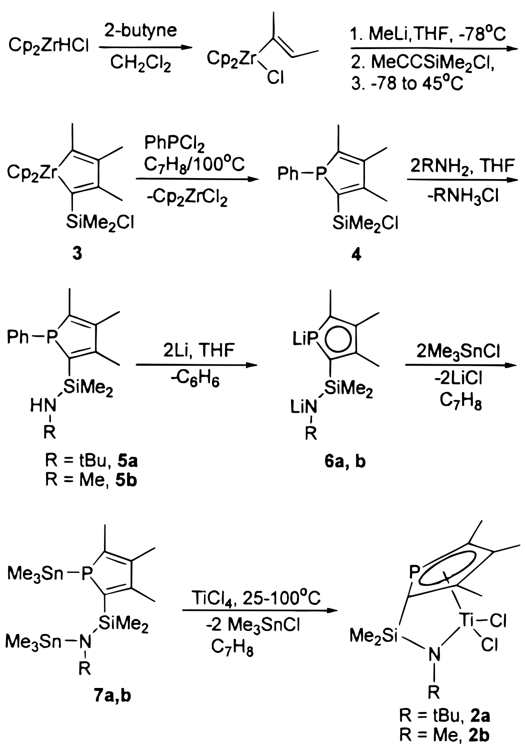
(7) Bis(phospholyl)zirconium complexes that act as bidentate ligands to Fe or W have been reported. See: Nief, F.; Mathey, F. Ricard, L. *J. Organomet. Chem.* **1990**, *384*, 384.

10.1021/om9807710 CCC: $15.00
Publication on Web 11/07/1998

quantitative yield after removal of Cp_2ZrCl_2 by filtration.[5b] Condensation of **4** with excess *tert*-butylamine or methylamine cleanly gave the phosphole−$SiMe_2$−amido ligands **5a** and **5b**, respectively. Compounds **5** were then reacted with lithium in THF to give dianions **6**. This last reaction has not been examined in detail, but **6** were expected via the reductive cleavage of the P−Ph bond[5a] and subsequent deprotonation of the amine by the phenyl anion. Compounds **6** were never isolated but used directly in further reactions.

Our attempts to prepare complex **2** directly from **6** and $TiCl_4$ were unsuccessful, likely due to redox chemistry.[11] However, treatment of **6** with 2 equiv of Me_3SnCl gave the distannyl ligands **7** in >90% purity, as determined by ^1H NMR spectroscopy. Distannyls **7** proved to be useful precursors to **2**.[11]

Scheme 1



Combining **7** with $TiCl_4$ in toluene gave Me_3SnCl elimination and yielded compounds **2**. In the case of *tert*-butyl derivative **7a**, heating of the reaction mixture to 100 °C was required to ensure complete reaction. However, for the less sterically encumbered methyl derivative **7b** the reaction went at 25 °C. Compounds **2** were isolated as orange crystalline solids in good yield (**2a**, 57%; **2b**, 95%, based on **5**) and were purified by crystallization from pentane.

Compounds **2** have been characterized by ^1H and ^{31}P NMR spectroscopy, elemental analysis, and in the case of **2a** by X-ray crystallography. A view of **2a** is given in Figure 1 with selected bond lengths and angles.[12] Of note, the presence of the $SiMe_2$ bridge in **2a** leads to a 108.4° phospholyl(centroid)−Ti−N angle and to a 0.9439 Å deviation of Si from the plane of the phospholyl ring. The angle is much narrower than the 115.7° centroid−Ti−Cl angle found in the unbridged (3,4,-dimethylphospholyl)titanium trichloride, **8**, the only other structurally characterized monophospholyltitanium complex.[13] This narrowing of the angle in **2a** is comparable to the results observed for compound **1** (Cp(centroid)−Ti−N, 107.6°; Si deviation, 0.87 Å) relative to unbridged monocyclopentadienyltitanium complexes (Cp(centroid)−Ti−N, 115−120°).[6] Compounds **2a** and **1** clearly share some basic structural features.

---

(8) Representative Experimental Procedures. Preparation of 3: To a slurry of Cp_2ZrHCl (3.802 g, 14.74 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added 2-butyne (2.5 mL, 1.72 g, 32 mmol). The reaction was allowed to warm to room temperature, and after 30 min a clear solution formed. The volatiles were removed in vacuo and the residues redissolved in THF (30 mL). The solution was cooled to −78 °C, and a solution of MeLi in ether (1.4M, 10.5 mL, 15 mmol) was added. After 15 min chloro(dimethyl)(propynyl)silane (1.955 g, 14.7 mmol) was added, and the reaction mixture was allowed to warm to room temperature. The reaction was stirred at 25 °C for 45 min, at 45 °C for 2 h, and then at room temperature overnight. The solvent was removed in vacuo, hexane (50 mL) added, and the reaction filtered. The filtrate was concentrated until crystals appeared and then cooled to −15 °C for 2 days. The orange crystalline product was isolated by decanting the mother liquor and drying in vacuo. Yield: 4.2 g, 69%. ^1H NMR (C_7D_8, δ): 6.01 (s, Cp*H*,10H), 1.78 (s, 3H), 1.65 (s, 3H), 1.53 (s, 3H), 0.50 (s, Si*Me*$_2$, 6H). Anal. Calcd (found) for $C_{19}H_{25}ClSiZr$: C, 55.93 (55.93); H, 6.13 (6.19). Preparation of 4: Compound **3** (4.028 g, 9.88 mmol), $PhPCl_2$ (1.771 g, 9.89 mmol) and toluene (50 mL) were combined, and the reaction mixture was refluxed for 3 h. The solvent was removed in vacuo, hexane (50 mL) was added, and the reaction was cooled to 0 °C. The reaction was filtered, the solvent removed in vacuo, and the product obtained as a dark orange oil. The oil was further purified by a second hexane extraction to remove residual Cp_2ZrCl_2. Yield: 2.99 g, 103% (a small amount of Cp_2ZrCl_2 remained). ^1H NMR (C_7D_8, δ): 7.27 (m, 2H), 7.00 (m, 3H), 2.17 (d, $J_{PH} = 4.4$ Hz, 3H), 1.81 (d, $J_{PH} = 11.6$ Hz, 3 H), 1.66 (d, $J_{PH} = 1$ Hz, 3H), 0.44 (d, $J_{PH} = 10.8$ Hz, 6H). $^{31}P\{^1H\}$ NMR (C_7D_8, δ): 31.6. Preparation of 5a: To a solution of **4** (1.358 g, 4.61 mmol) in THF (30 mL) at −78 °C was added *tert*-butylamine (1.3 mL, 12.4 mmol). A white precipitate formed immediately, and the reaction was warmed to room temperature. After 1 h the volatiles were removed in vacuo, and hexane (10 mL) was added. The reaction was filtered, the solvent removed in vacuo, and the product isolated as an orange oil. Yield: 1.483 g, 97%. ^1H NMR (C_7D_8, δ): 7.3 (m, 2H), 7.0 (m, 3H), 2.25 (d, $J = 3.7$ Hz, 3H), 1.9 (d, $J_{PH} = 10.7$ Hz, 3H), 1.78 (m, 3H), 1.08 (s, *t*Bu, 9H), 0.27 (d, $J_{PH} = 0.9$ Hz, Si*Me*$_2$, 6H). $^{31}P\{^1H\}$ NMR (C_7D_8, δ): 31.5. Preparation of 2a: A solution of **5a** (1.465 g, 4.4 mmol) in THF (30 mL) was added to Li foil (163 mg, 143 mmol) at room temperature and the reaction stirred for 3 h. The resulting dark red solution was then filtered into a solution of Me_3SnCl (2.04 g, 10 mmol) in THF (20 mL) at −78 °C. After warming and stirring for 1 h at room temperature, the solvent was removed in vacuo, and residues analyzed by ^1H NMR spectroscopy. The NMR spectrum showed that the distannyl product, **7a,** had formed in >90% purity. ^1H NMR (C_7D_8, δ): 2.48 (d, $J_{PH} = 1.1$ Hz, 3H), 2.2 (d, $J_{PH} = 12.2$ Hz, 3H), 1.92 (s, 3H), 1.26 (s, 9H), 0.48 (s, 6H), 0.38 (s, 9H), 0.07 (d, $J_{PH} = 1.8$ Hz, 9H). $^{31}P\{^1H\}$ NMR (C_7D_8, δ): −27.3. A solution of **7a** (4.4 mmol) in toluene (30 mL) was added to a toluene solution of $TiCl_4$ (835 mg, 4.4 mmol) at 0 °C. The reaction turned dark red immediately, and it was left to stir overnight. The toluene and other volatiles were removed in vacuo, and an ^1H NMR spectrum of the residue showed a mixture of products. The oil was redissolved in toluene (50 mL) and heated to 100 °C for 1 h. The volatiles were removed in vacuo to leave a crystalline solid. The solid was dissolved in pentane (40 mL) and the solution filtered and cooled −30 °C for 2 days. Orange/red crystals formed, and these were isolated by decanting the mother liquor, washing with pentane, and drying in vacuo. Yield: 916 mg, 57%. ^1H NMR (C_7D_8, δ): 2.22 (d, $J_{PH} = 10$ Hz, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.36 (s, 9H), 0.57 (d, $J_{PH} = 1.62$ Hz, Si*Me*Me, 3H), 0.43 (s, SiMe*Me*, 3H). $^{31}P\{^1H\}$NMR (C_7D_8, δ): 37.8. Anal. Calcd (found) for $C_{13}H_{24}Cl_2NPSiTi$: C, 41.96 (41.92); H, 6.57 (6.30); N, 3.77 (3.86).

(9) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(10) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870.

(11) Nief, F.; Mathey, F. J. *J. Chem. Soc., Chem. Commun.* **1988**, 770.

(12) Crystal data for **2a**. $C_{13}H_{24}Cl_2NPSiTi$, monoclinic, $C2/c$, $a = 16.010(1)$ Å, $b = 19.799(2)$ Å, $c = 12.191(1)$ Å, $\beta = 104.706(2)°$, $V = 3737.9(6)$ Å^3, $Z = 8$, $D_{cald} = 1.323$ g cm^{-3}, $\mu = 0.882$ mm^{-1} (Mo Kα, $\lambda = 0.710\ 73$ Å), $F(000) = 1552$; 6982 reflections (θ range = 1.67−22.50°) at 296 K, 2432 unique data ($R_{int} = 0.0403$), transmission 0.3493−0.2756 for crystal size 0.40 × 0.40 × 0.40 mm. Final $R_1 = 0.055$, $R_2 = 0.1195$. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer collecting a hemisphere of data in 1329 frames with 10 s exposure times. The data were processed using the SAINT and XPREP processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI Indy computer.

(13) Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **1989**, *8*, 1473.

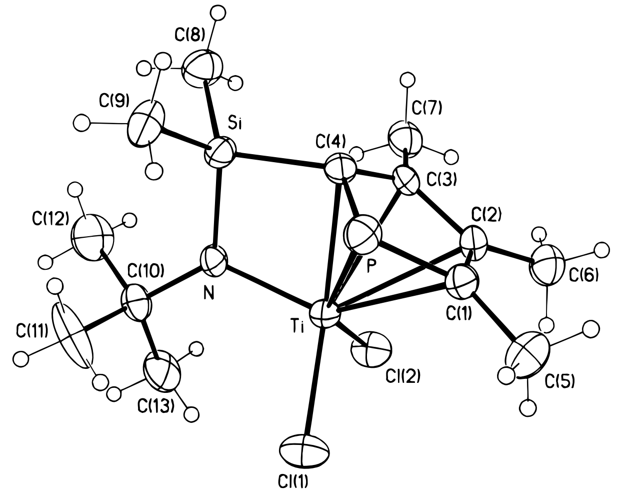


Figure 1. Crystallographic view of compound **2a**. Selected bond lengths (Å) and angles (deg): Ti−C(1) 2.543(5), Ti−C(2) 2.522(5), Ti−C(3) 2.407(5), Ti−C(4) 2.324(5), Ti−P 2.599(2), Ti−N 1.909(4), N−Si 1.765(4), Si−C(4) 1.873(5). Cl(1)−Ti−Cl(2) 102.00(7), Ti−N−C(10) 127.5(3), Ti−N−Si 105.7(2), N−Si−C(4) 91.2(2), Si−C(4)−P113.9(3), Si−C(4)−C(3) 124.8(4), C(4)−C(3)−C(2) 110.8(5), C(4)−P−C(1) 89.8(3), P−C(1)−C(2) 113.1(4), C(1)−C(2)−C(3) 113.2(5).

Preliminary ethylene polymerization data[14] for compounds **2** show substantially improved catalyst activity relative to the essentially inactive unbridged mono(η^5-2,3,4,5-tetramethylphospholyl)titanium trichloride,[11] **9** (Table 1). Perhaps more surprisingly, the data also show similar activities for compounds **2a** and **1**. The utility of this interesting result was somewhat offset by the lower M_w PE obtained from compounds **2** compared to compound **1** under the reaction conditions described. Explanation of this lower M_w result requires further study but increases in polymer M_w can be obtained from compounds **2** by decreasing reactor temperature and increasing ethylene concentration (ethylene flow).[15] Methyl derivative **2b** gave lower catalyst activities than **2a**. Similar activity decreases were reported for the methyl derivative of compound **1**.[6]

Table 1. Ethylene Polymerization Data for Compounds 1, 2, and 9 with MAO Activation

catalyst	ethylene flow (g/min)	temp (C)	activity[a] kg(PE)/(mmol × min)	M_w ($\times 10^{-3}$)	M_w/M_n
2a	1.0	160	18.0	29	6.3
2a	2.1	160	41.1	50	2.8
2a	1.0	140	18.8	45	3.2
2b	1.0	160	10.7	40	2.7
2b	2.1	160	26.4	70	3.5
1	1.0	160	17.7	73	4.6
1	2.1	160	41.3	126	4.2
1	1.0	140	19.3		
9	1.0	160	<0.1		

[a] Catalyst activity under steady-state conditions.

By the introduction of a bridged ligand structure, we have shown significantly increased catalyst activity is available from monophospholyltitanium complexes. We have also discovered striking similarities in the crystal structures and polymerization activities of compounds **2a** and **1**. These results show the benefits of transferring ligand design technologies developed for metallocene catalysts to other ligand systems and further demonstrate the potential of the phospholyl ligand as a cyclopentadienyl substitute.

Acknowledgment is made to the Analytical Department at NOVA Research & Technology Corp. for assistance with chemical characterization data.

Supporting Information Available: Tables of complete crystallographic data for **2a** and the preparative details for MeC≡CSiMe$_2$Cl, **5b**, and **2b** (8 pages). Ordering information is given on any current masthead.

OM9807710

---

[14] Polymerization experiments were conducted in a stainless steel reactor at 1500 psi. Cyclohexane, catalyst and ethylene were continuously added to the reactor, and the product was continuously removed. Toluene solutions of catalysts (1.0 mM) and methylalumoxane (Akzo Nobel, 400 mM) were pumped at 1.0 mL/min into the reactor, to give an Al/Ti ratio of 400 mol/mol. The total flow of solvent to the reactor was 27 mL/min. On exiting the reactor, nonanoic acid was added to prevent further polymerization. The ethylene conversion was measured by GC reference to an internal standard (propane). Polymer samples were analyzed by high-temperature GPC.

[15] The fact that **2b** gave higher M_w polymer than **2a** is likely a function of lower catalyst activity leading to a higher effective ethylene concentration.